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PATENT SPECIFICATION

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| 27th October, 1965. | | |

Complete Specification
Entitled

PROCESS FOR THE PREPARATION OF ESTERS OF
HYDROXYPHENYL ALKANOIC ACIDS.

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Convention Priority

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Applicant

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09.10; 47.7; 09.2; 20.6.

The following statement is a full description of this invention, including the best method of performing it known to us :

26-ND-6/3/69-5P, C

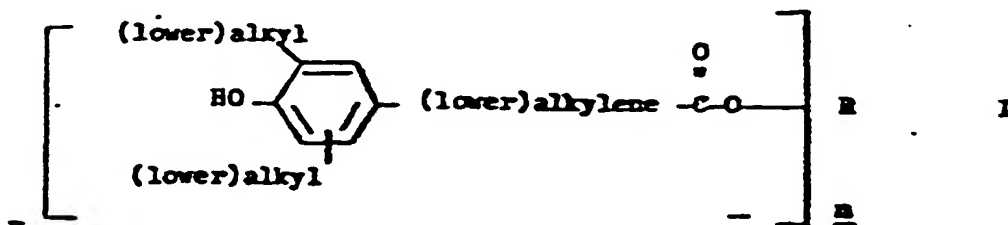
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The present invention relates to a novel process for the preparation of organic esters and in particular to various esters of hydroxyphenyl(lower) alkanolic acids.

There are obtained according to the present invention, esters of the formula:



in which n has a value of from one to six and

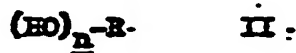
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in which R is non-hydroxylated saturated residual radical of an organic compound having n hydroxy groups, whereby each valence of the radical is on a separate carbon atom selected from the group consisting of straight and branch chain aliphatic hydrocarbons containing from one to thirty carbon atoms whereby n is one to six, cycloaliphatic hydrocarbons containing from five to seven carbon atoms, whereby n is five to seven and straight and branch chain aliphatic mercapto-hydrocarbons containing from four to forty carbon atoms and from one to three non-terminal sulfide links, whereby n is four to six.



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The compounds prepared according to the present invention are thus di-(lower)alkylhydroxyphenyl(lower)-alkanoic acid esters of mono- and polyhydric alcohols, which alcohols have the formula:



where R and n are as above defined.

The compounds of FORMULA I are economical and superior stabilizers for organic matter normally subject to deterioration such as synthetic organic polymeric substances, e.g., polypropylene, polystyrene and polyethylene; animal and vegetable-derived oil; hydrocarbon oils; aliphatic ester lubricants; and the like.

With greater particularity, R may be the monovalent branch or straight chain saturated hydrocarbon radical of a monohydric alcohol of from one to thirty, preferably six to twenty, carbon atoms, such as for example butyl alcohol, hexyl alcohol, octyl alcohol, decyl alcohol, dodecyl alcohol, tetradecyl alcohol, octadecyl alcohol, eicosyl alcohol and the like. R may also be the polyvalent branch or straight chain hydrocarbon radical of a polyhydric alcohol of from two to thirty, preferably two to six, carbon atoms, such as for example ethylene glycol; 1,2-propane glycol; 1,3-propane glycol; 1,4-butanediol; 1,6-hexanediol; 1,2-octanediol; 1,7-hepanediol;

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1,2,3-butanetriol; glycerol; neopentyl glycol; erythritol; pentaerythritol; dipentaerythritol; sorbitol; 2,5-hexanediol; 1,1,1-trimethylolethane; 1,1,1-trimethylolpropane; 2,2,4-trimethyl-1,3-pentanediol and the like.

R may also be the mono- or polyvalent saturated alicyclic hydrocarbon radical of a mono- or polyhydric alcohol of from five to seven carbon atoms such as cyclopentanol, 1,3-cyclohexanediol, inositol and the like.

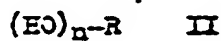
R may also be the mono- or polyvalent branch or straight chained saturated hydrocarbon radical of mercapto alcohol containing from one to three non-terminal sulfide links and from four to forty carbon atoms. By the designation "non-terminal sulfide links" is intended a sulfide bond between two carbon atoms, neither of which is otherwise a terminal carbon atom in its respective hydrocarbon chain. Necessarily therefore a two carbon segment will be bound to each bond of the sulfide links so designated. Representative of such alcohols are thus ethylmercaptoethanol, 2,2'-diethanol sulfide, 2-hydroxyethyl n-octyl sulfide, 3-hydroxypropyl n-dodecylsulfide, n-octylthioethylthioethanol, 2,2'-di-(n-hexadecylthiomethyl)-1,3-propanediol and the like.

By the term "alkyl" and derivations thereof, such as "alkanoic", "alkanol", and "alkylene", when used in regard to the present invention, is intended

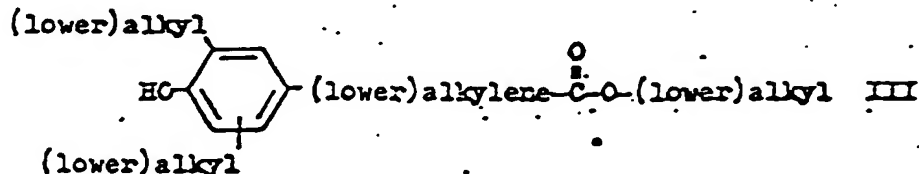
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a group comprising branch or straight chain hydrocarbon group of from one to about thirty carbon atoms. When qualified by the term "(lower)", the hydrocarbon group will contain from one to about six carbon atoms. With particular reference to the two (lower)alkyl groups of the di-(lower)alkylhydroxyphenylalkanoyloxy moiety of the compounds prepared herein, one or both of these are preferably branch chain hydrocarbons such as t-butyl, although not limited to such. Thus such arrangements as 2-methyl-4-hydroxy-5-t-butylphenyl are also envisioned. At least one of these (lower)alkyl groups is in a position ortho to the hydroxy group while the second is either in the position ortho in the hydroxy group or the position meta to the hydroxy group and para to the first (lower)alkyl group.

According to this invention, compounds of FORMULA I are prepared by treating a mono- or polyhydric alcohol of the formula:



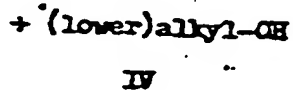
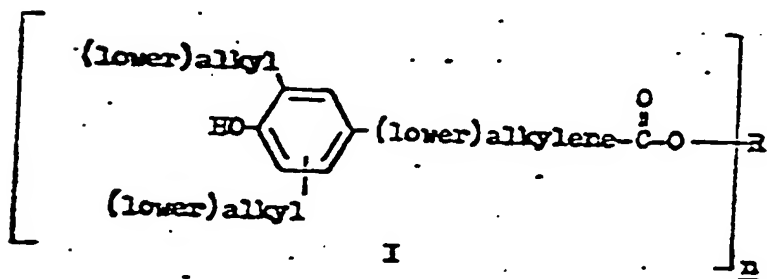
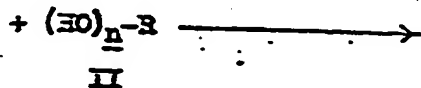
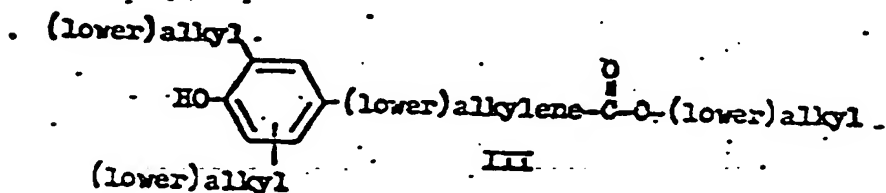
with at least a stoichiometric amount, i.e., at least n molar equivalents and preferably from a $.05n$ to a $.15n$ excess over the molar equivalent amount, of an ester of the formula:



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in the presence of a hydride of an alkali metal or alkaline earth metal, as for example, lithium hydride, sodium hydride, calcium hydride, magnesium hydride and the like. Of the metal hydrides, lithium hydride is particularly advantageous. The metal hydride is employed in an amount which is from about 0.05 \underline{n} to about 0.15 \underline{n} molar equivalents of the amount of the alcohol of FORMULA II which is employed.

The reaction which is utilized in this process may be schematically represented as follows:



In this reaction equation, \underline{n} and R are as above defined. Preferably the starting ester (III) is the methyl ester of β -[3,5-di-(lower)alkyl-4-hydroxy-

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phenyl] propionic acid, the (lower) alkanol formed (IV) thus being methanol.

The process of this invention utilizes reaction temperatures of from 70°C to 150°C; preferably from 90°C to 120°C, and pressures at or below atmospheric pressure. Since the reaction is facilitated through removal of the (lower) alkanol (IV) generated, an initial reaction phase is conducted at a pressure at least as low as the vapor pressure of the (lower) alkanol (IV) in the reaction mixture at the reaction temperature. Depending upon the particular reactants and whether or not a solvent is employed, this may be atmospheric pressure or below. The (lower)-alkanol (IV) thus generated is removed from the reaction environment, as by condensation, so as to facilitate completion of the reaction. Although not necessary, this (lower) alkanol may be collected so as to provide estimates of the degree of completion of the reaction and rate of production. Generally from 50% to 90%, typically 75%, of the theoretical amount of the (lower) alkanol (IV) can be thus isolated. This initial reaction phase is continued until the generation of the (lower) alkanol (IV) is substantially terminated. Thereafter the reaction is subjected to a terminal reaction phase wherein by the use of temperatures above those of the initial reaction phase and reduced pressure, the reaction is driven substantially to completion. The period of this terminal reaction phase is determined by the rate of production, as evaluated for example by vapor phase chromatography, until from 90% to 100%, typically 95%, of the theoretical yield of the product

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is observed. Generally this takes from two to ten hours although this may vary.

The process may be executed in the presence or absence of a solvent. In the case of those low melting alcohols of FORMULA II which are liquid at the reaction temperature, a solvent is not necessary, although improvements in the quality and yield of the product are often observed by the use of a solvent. In the case of high melting alcohols, e.g., those melting at or above 150° C, the use of a solvent is generally desirable. In one embodiment of this invention, the solvent may take the form of the final product itself. Alternatively, the solvent may be any alkali-inert non-aqueous organic solvent, preferably one having a vapor pressure over the reaction temperature range less than the vapor pressure of the (lower)alkanol (IV) formed. Suitable solvents thus include, among others, dimethylsulfoxide, tetra-hydrofuran, dioxane, pyridine, dimethylformamide, dimethylacetamide, nitrobenzene, o-nitroaniline and the like.

When a solvent is employed, an intermediate reaction phase may be employed for removal of the solvent since the solvent is primarily directed towards solubilizing high melting reactants during the initial reaction phase. Generally after the substantial transesterification which occurs during the initial reaction phase, any remaining reactants are sufficiently soluble in the fully or partially esterified materials already formed to eliminate the need for the solvent. Thus the solvent need only have a vapor pressure at least as low as the vapor pressure of the (lower)alkanol (IV), but

preferably lower, in the reaction mixture at the reaction temperature so as to perform its solubilizing function during the generation of (lower)alkanol (IV) and the concurrent formation of esterified material.

Because of the possibility of generating molecular hydrogen through the presence of the metal hydride, it is generally desirable to employ an inert atmosphere, such as nitrogen, and anhydrous conditions. The order of addition of reactants is not critical and can usually be adjusted to the convenience of a skilled operator. Upon completion of the reaction, the mixture is neutralized by the addition of an acid, as for example, acetic acid. The product is then collected and purified by the usual methods.

Occasionally, and notwithstanding the use of conditions designed to remove the reaction solvent by distillation, traces of solvent may remain more or less associated with the product. These may be readily removed by azeotropic distillation, extraction, drying or like methods. Thus, for example, if traces of dimethylsulfoxide, the preferred solvent, remain associated with the product after completion of the reaction and extraction with an isolation solvent such as heptane, the solution may be extracted with hot water, the aqueous extracts removing the dimethylsulfoxide while the product remains in the hydrocarbon.

In certain instances, as for example with tetra-[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionoylmethyl]-methane, the tendency to retain solvent appears to be traceable to the formation of lattice complexes. This can be observed

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with a number of different solvents ranging from (lower) alkanols such as isopropanol to halogenated hydrocarbons such as carbon tetrachloride. These complexes can be isolated as such and demonstrate distinct chemical and physical properties. Indeed it is often possible to advantageously utilize the different compatibilities of these in various substrates. As indicated above however, the complexes may be readily converted to the unassociated product.

While this process has general applicability for the preparation of an ester of FORMULA I, it is particularly valuable for polyhydric alcohols such as pentaerythritol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpentane, and the like which are difficult to prepare by classical esterification methods. On the basis of the properties of the final product, the preferred application of this process involves the use of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and pentaerythritol with lithium hydride to produce tetra-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy-methyl]methane. The process can also be successfully employed for the preparation of esters of higher molecular weight polyhydric compounds such as those of polyvinyl alcohol.

The reactants of FORMULA II may be prepared by a number of different routes including direct esterification. One particularly valuable route for preparing propionate reactants of this formula, involves the condensation of a dialkylphenol with a (lower)alkyl acrylate in the presence of a base such as potassium t-butoxide. Other methods, some of which are exemplified hereafter, are of course available.

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The following examples, presented by way of illustration and not limitation, will serve to further exemplify the nature of this invention. In these examples, parts are by weight unless otherwise specified and the relation of parts by weight to parts by volume is as that of grams to cubic centimeters.

EXAMPLE 1

Methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate

To 500 parts by volume of dry t-butyl alcohol in a reaction vessel fitted with mechanical stirrer, inert gas inlet, thermometer, condenser and dropping funnel are added 2.1 parts of potassium metal. After the ensuing reaction is complete, 37.3 parts of 2,6-di-t-butylphenol are added, followed rapidly by 17.7 parts of methyl acrylate. The reaction mixture is stirred at 50°C for 18 hours and allowed to cool. The solvent is then removed under reduced pressure and the residual mass neutralized by addition of dilute hydrochloric acid. This mixture is next extracted with two portions of 200 parts by volume each of ethyl ether. The combined ethereal extracts are washed with two portions of 100 parts by volume of water, dried over anhydrous sodium sulfate and concentrated on a steam bath. The residual oily mass is distilled in vacuo, the fraction collected at 125-130°C/0.1mm crystallizing upon standing to yield methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, m.p. 63.0-64.5°C. Recrystallization from hexane yields a white solid, m.p. 66.0-66.5°C.

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| | C | H | Saponification Equivalent |
|-------------------------------|-------|------|------------------------------|
| Calc. for $C_{18}H_{28}O_3$: | 73.93 | 9.65 | 292.4 |
| Found: | 74.27 | 9.90 | 292±10 |

In a similar fashion, the corresponding (lower)-alkyl esters are obtained by using ethyl, propyl, butyl, amyl and hexyl acrylate in place of methyl acrylate. These various esters may be employed in molar equivalent amounts in place of the methyl ester which is exemplified in the following examples.

By employing 2-methyl-6-t-butylphenol in place of 2,6-di-t-butylphenol in this procedure, there is obtained methyl 3-(3-methyl-4-hydroxy-5-t-butylphenyl)propionate, b.p. 136-144°C/0.02 mm.

Other phenolic substituted (lower)alkanoate starting materials may be obtained for example as follows:

(a) To 200 parts by volume of dry t-butyl alcohol in suitable reaction vessel, fitted with mechanical stirrer, inert gas inlet, thermometer, condenser and dropping funnel, are added 22.4 parts of potassium t-butoxide, 41.2 parts of 2,6-di-t-butylphenol and 50 parts by volume of triethylene glycol dimethyl ether. The dark green solution is stirred while a solution of an equimolar portion of ethyl -bromo- - methylpropionate in 50 parts of t-butyl alcohol is added dropwise over a 60 minute period. After the addition is complete, the reaction mixture is refluxed for 1 hour, poured into water and extracted with ether. The ethereal extracts are washed with water, dried and evaporated, the residue, ethyl 2-(4-hydroxy-3,5-di-t-butyl-phenyl)isobutyrate, being further purified by vacuum distillation.

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(b.) Anhydrous gaseous hydrogen chloride is bubbled through an ethanolic solution of 24.5 parts of 3,5-di-
t-butyl-4-hydroxybenzylcyanide at 0-5° for 4 hours and then
at 20-25° for 2 hours. The reaction mixture is
allowed to stand overnight and then poured with stirring
into 600 parts of water at 25°. The oily dispersion
is heated at 60-65° for 1 1/2 hours, cooled to room
temperature and extracted with two

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portions of 200 parts by volume of benzene. The benzene extracts are in turn washed with two portions of 100 parts by volume of water and two portions of 100 parts by volume of saturated aqueous sodium bicarbonate. After removal of benzene, the residual product is purified by distillation to yield ethyl (3,5-di-*t*-butyl-4-hydroxyphenyl)acetate, b.p. 111-113°/0.08-0.10 mm, which solidifies upon standing, m.p. 48-49°.

(c.) Seventeen parts of 3,5-di-*t*-butyl-4-hydroxyphenylacetic acid and 0.5 parts of *p*-toluene-sulfonic acid are dissolved in 200 parts by volume of methanol and heated under reflux for 3 hours. The brown reaction mixture is poured onto crushed ice and the precipitated methyl ester filtered by suction. The filter cake is dispersed in saturated bicarbonate solution, filtered, washed neutral with distilled water and dried.

Methyl 3,5-di-*t*-butyl-4-hydroxyphenylacetate, m.p. 79-83° is thus obtained and further purified by distillation, b.p. 117-118°/0.1-0.05 mm followed by recrystallization from hexane:petroleum ether, final m.p. 85-86.5°.

Calc. for $C_{17}H_{26}O_3$:

C, 73.34; H, 9.41

Found:

C, 73.53; H, 9.17

Methyl 6-(3,5-di-*t*-butyl-4-hydroxyphenyl)hexanoate is prepared in an analogous manner from 6-(3,5-di-*t*-butyl-4-hydroxyphenyl)hexanoic acid.

In the following examples, methyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate is utilized as the starting ester. Other (lower) alkyl di-(lower) alkyl-4-hydroxyphenyl (lower) alkanoates, such as those prepared in this example, in equivalent quantities, can be alternatively employed.



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EXAMPLE 2

Tetra-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxymethyl]-methane

(a.) Pentaerythritol (6.8 parts) and lithium hydride (0.0885 parts) are added to a reaction vessel equipped with an agitator, Dean-Stark trap and nitrogen inlet. The mixture is heated until the contents are molten (about 220°C) and then cooled below 50°C. Methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (64.5 parts) is then added and the reaction mixture heated at 185-190°C for 13 hours with stirring. During this time, nitrogen is continuously introduced to provide an inert atmosphere and remove the generated methanol. The reaction mixture is then cooled and 500 parts of benzene are added. The mixture is neutralized with glacial acetic acid and heated until a nearly complete solution is realized. After clarification by filtration, the reaction mixture is heated under reduced pressure to remove the solvent, cooled, then treated with 400 parts by volume of hexane and filtered. Chromatography over neutral alumina with elution with hexane produces an initial yellow impurity followed by the desired product which is freed of solvent by evaporation. The product, when obtained according to this procedure, appears as a clear amber glass which softens at 50-60°C.

| | |
|-----------------------------------|-------------------|
| Calc. for $C_{73}H_{108}O_{12}$: | C, 74.45; H, 9.24 |
| Found: | C, 74.62; H, 9.33 |

(b.) Alternatively this process may be executed in the presence of solvent by slurrying 6.8 parts of pentaerythritol with 50 parts by volume of dimethyl sulfoxide and first addition 0.177 parts of lithium



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hydride, followed by 64.5 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate. The reaction mixture is heating at 85-90°C/15-20 mm with stirring until methanol is no longer evolved. The solvent is then removed under diminished pressure and the cooled residue dissolved in 300 parts by volume of benzene. Glacial acetic acid is added to neutralize the mixture, which is then filtered to remove a small quantity of insoluble material. The filtrate is washed with water until neutral, then dried over sodium sulfate, filtered and stripped of solvent. The residue is freed of unreacted starting ester by distillation, 120-140°C/0.1 mm. The residue thus comprises the product.

(c.) As another variation in this process a reaction vessel is equipped with a thermometer, stirring apparatus and distillation condenser. The vessel is purged with nitrogen and 128.6 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 13.6 parts of pentaerythritol and 80 parts by volume of dimethyl sulfoxide are added and stirred until a homogeneous mixture is obtained. The system is evacuated to about 10-20 mm and 20% of the initial volume of dimethyl sulfoxide is removed by distillation in order to dry the reagents, solvent and apparatus. The reaction mixture is then cooled to at least 50°C and the vacuum broken by the introduction of dry nitrogen. There is then rapidly added with stirring, 0.177 parts of lithium hydride. The system is purged with nitrogen to entrain any molecular hydrogen which may be generated. The mixture is stirred for 10-15 minutes and then heated for from 2 to 3 hours at 80-90°C/20 mm. During this period, the methanol which is generated by the reaction

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is removed, 50% of the theoretical amount being generated during the first hour and about 75% of a theoretical amount being generated over the entire period.

The reaction mixture is then heated for 2 to 3 hours at a temperature of from 90-100°C and at a pressure sufficiently reduced to effect distillation of dimethyl sulfoxide.

At the end of this time, the reaction mixture is heated for an additional 2 to 3 hours at 100-120°C/5 mm or less.

The reaction mixture is cooled to about 80°C (or to such temperature as will maintain the mixture's mobility), neutralized with stirring by the addition of glacial acetic acid and stirred for 10-15 minutes. Four hundred and fifty parts by volume of heptane are added and stirring and heating are continued until a practically complete solution is obtained. In the event a complete solution is not obtained, the hot heptane solution may be washed with hot water. The heptane solution is then allowed to cool and the solid which forms is collected by filtration, washed with cold hexane and dried to obtain tetra-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionylacryethyl]methane, m.p. 119-122°C. Depending upon the conditions of isolation and solvent employed, it appears that this product can exist in a number of different forms. It forms a glass upon solidification of the hot reaction product, a high melting form (119-122°C) when crystallized from heptane, and a low melting form (80-90°C) when crystallized from cyclohexane.

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EXAMPLE 3

1,1,1-Tris-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxymethyl] propane

To a reaction vessel as described in Example 2 are added 585 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 67.1 parts of 1,1,1-trimethylolpropane and 1.33 parts of lithium hydride. The reactants are heated at 125-150°C for 1 1/2 hours at atmospheric pressure under nitrogen and then for an additional 4 hours at 110-120°C at 0.2-0.5 mm. One thousand parts by volume of hexane are added after cooling and the mixture then warmed with stirring and filtered. The stirred filtrate is treated with 15 parts by volume of glacial acetic acid, followed by an excess of sodium carbonate. After refiltering, the filtrate is freed of solvent and volatile impurities by slowly heating to 152°/0.22 mm. The product is obtained as a glass which softens between 55-70°C.

Calc. for $C_{57}H_{86}O_9$:

C, 74.80; H, 9.47

Found:

C, 74.45; H, 9.25

EXAMPLE 4

1,2,3,4,5,6-Hexa-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]hexane

By employing 9.1 parts of sorbitol, 0.239 parts of lithium hydride and 96.6 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate in 50 parts by volume of dimethyl sulfoxide in the second alternative procedure of Example 2, there is obtained 1,2,3,4,5,6-hexa-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]hexane.

CONVEX

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EXAMPLE 5

1,2,3-Tris-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]butane

The compound of this example is obtained according to the procedure of Example 2(b.) employing 10.6 parts of 1,2,3-butanetriol, 0.239 parts of lithium hydride and 97.1 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate in 50 parts by volume of dimethyl sulfoxide.

EXAMPLE 6

1,2-Bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethane

Calcium hydride (0.84 parts) is slowly added to 6.21 parts of ethylene glycol under an atmosphere of nitrogen in a reaction vessel fitted with a Dean-Stark trap. The mixture is heated to 110°C and cooled and 73.1 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate are added, maintaining the nitrogen atmosphere. An initial reaction temperature of 132°C gradually rises to 159°C over a 5 hour period during which time, 5.5 parts by volume of methanol are collected.

The reaction mixture is next heated for 5 1/2 hours at a bath temperature of 155-160°C/0.2-1 mm, cooled to room temperature and neutralized by the addition of 3 parts by volume of glacial acetic acid. The mixture is heated under reduced pressure to remove a small amount of excess starting ester and the residue then recrystallized from isopropyl alcohol, collected by filtration, and dried to yield 1,2-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-ethane, m.p. 142-144°C.



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Alternatively, 0.354 parts of lithium hydride and 6.21 parts of ethylene glycol are combined under nitrogen and allowed to react until the exothermic reaction has subsided. There are then added 64.33 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate. This mixture is heated with stirring, the methanol evolved being swept out by the nitrogen and collected in a Dean-Stark trap. An initial temperature of 76°C is allowed to rise to 105°C over a period of approximately 5 1/4 hours. The mixture is then allowed to cool and neutralized by addition of 3 parts by volume of glacial acetic acid. The neutralized mixture is next heated at atmospheric pressure until molten and distilled in vacuo, an initial fraction being collected at about 55-60°C/1.8 mm and a second fraction being collected at about 135-144°C/0.2 mm. The residue is dissolved in 150 parts by volume of isopropanol, treated with diatomaceous earth and filtered. Upon standing, the product crystallizes and this material is filtered under vacuum, washed once with 40 parts by volume of isopropanol and dried to yield 1,2-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethane.

EXAMPLE 7

1,4-Bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]butane

1,4-Butanediol (9.01 parts) and 0.0885 parts of lithium hydride are combined under nitrogen. When the exothermic evolution of gas has subsided, 64.33 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate are added. The reaction is heated with stirring from an initial temperature of 84°C to a final temperature of 109°C over a period of 2 1/2 hours during which time 4.4 parts by volume of methanol are collected. The mixture

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is then heated for an additional 2 1/2 hours at 150-160°C/0.5 mm and then partially cooled and neutralized by the addition of 1.2 parts by volume of glacial acetic acid. The unreacted starting material is removed by vacuum distillation, b.p. 127°C/0.14 mm, and the residue dissolved in 100 parts by volume of isopropanol, treated with diatomaceous earth and filtered. The solid which precipitates from the filtrate upon standing is freed of solvent under reduced pressure and dried to yield 1,4-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-butane, m.p. 82-84°C.

EXAMPLE 8

2,2-Bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxymethyl]propane

To a reaction product of 20.8 parts of neopentylglycol and 0.0885 parts of lithium hydride are added under nitrogen 123.3 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate. The reaction mixture is heated under the nitrogen atmosphere for approximately 2 1/2 hours at from 105-122°C during which time 7.9 parts of methanol are collected. The reaction mixture is then heated for an additional hour at 120°C/0.2-0.5 mm, cooled to room temperature and neutralized to the addition of 0.6 parts by volume of glacial acetic acid. The resulting mixture is dissolved in 600 parts by volume of hexane, treated with diatomaceous earth, filtered and evaporated. The residue is recrystallized from 95% ethanol and thoroughly dried to yield 2,2-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxymethyl]propane, m.p. 81-82°C.

EXAMPLE 9

3-(Dodecylthio)propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate

To a reaction mixture of 41.2 parts of



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n-dodecylthiopropenal and .070 parts of lithium hydride are added under nitrogen 43.8 parts of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate. The reaction mixture is heated for approximately 2 hours at a reaction temperature of from 99-114°C. During this time, 5.2 parts by volume of methanol are collected. The mixture is then heated for an additional 1 1/4 hours at 120-125°C/0.1-0.5 mm, cooled to room temperature and neutralized with 0.6 parts by volume of glacial acetic acid. The reaction mixture is then dissolved in 400 parts by volume of hexane, treated with diatomaceous earth and filtered. The filtrate is evaporated in vacuo and purified in a molecular still at 260-270°C/1-3 to yield 3-(dodecylthio)propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, calculated: C, 73.78; H, 10.83; S, 6.15; found: C, 73.63; H, 10.65; S, 6.14.

EXAMPLE 10

The following tabulated series of experiments employing methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate as the starting ester and lithium hydride will further serve to typify the nature of this invention.



| MOLAR | | METHANOL | | | | | | | | | | | | | | | |
|---|---------------|--------------------------|--------------------------|---------|--------------------------------|------------------|-------|---------------------------------|---------|--|-------|-------|---------|--|--|--|--|
| MOLAR | | METHANOL | | | | | | | | | | | | | | | |
| AMOUNT | HYDRIDE ESTER | AMT. OF LITHIUM STARTING | AMT. OF LITHIUM STARTING | SOLVENT | HEATING (X OF | COLLECTED SECOND | THIRD | HEATING | HEATING | THEORY | PHASE | PHASE | PRODUCT | | | | |
| Inositol/0.05 | 0.03 | 0.33 | 0.33 | DM80 | 60-85°/ 14-20mm/ 10 hrs. | 69.5 | -- | 116°/ 0.1-0.2mm/ 45 min. | -- | 1,2,3,4,5,6-hexa-[3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionyloxy]cyclohexane, m.p. 205-208°. | | | | | | | |
| Glycerol/0.10 | 0.015 | 0.33 | 0.33 | -- | 87-115°/ 17mm/ 13.5 hrs. | 74.0 | -- | 125°/ 0.2-0.4mm/ 7.5 hrs. | -- | 1,2,3-tris-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]propane, softens 40-60°. | | | | | | | |
| 2,2-bis-(hexa-decylthio-methyl)-1,3-propanediol/ 0.029 | 0.0029 | 0.064 | 0.064 | -- | 98-114°/ ATM./ 4 hrs. | 68.5 | -- | 115°/ 0.1mm/ 3 hrs. | -- | 2,2-bis-(hexadecylthio-methyl)-1,3-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]propane, Calor: 0, 74.94; H, 10.93; Found: 8, 5.63; 6, 74.90; 8, 10.81. | | | | | | | |
| N-octylthio-ethylthio-ethanol/ 0.040 | 0.004 | 0.004 | 0.004 | -- | 78-83°/ ATM./ 2.7 hrs. | 81.5 | -- | 95°/ 0.2mm/ 1. hrs. | -- | N-octylthioethylthioethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, Calor: 0, 68.18; H, 9.87; Found: 8, 12.55; 0, 67.96; 8, 9.69; 8, 12.57. | | | | | | | |

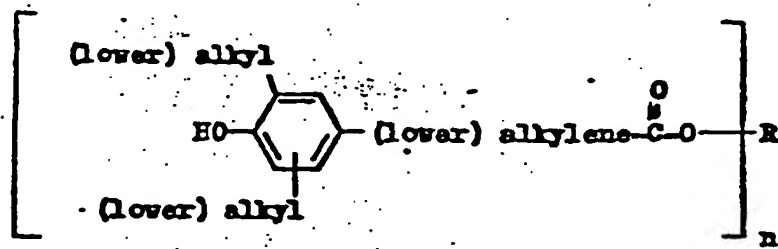


| MOLAR | | METHANOL | | | | | |
|-----------------|---|------------------|---------|----------------------------------|--------------------------------------|-----------------------------|--|
| AMT. OF AMT. OF | FIRST | COLLECTED SECOND | THIRD | | | | |
| ALCOHOL/MOLAR | HEATING | (% OF | HEATING | | | | |
| AMOUNT | PHASE | THEORY) | PHASE | | | | |
| HYDRIDE ESTER | THEORY) | PHASE | PHASE | | | | |
| 5 | 1,4-dimethyl- cyclohexane/ 0.10 | 0.01 0.22 | -- | 99-119°/ ATM. 2.5 hrs. | 145-150°/ 0.1mm/ 0.5 hrs. | -- | 1,4-bis-[3-(3,5-di-t-butyl- 4-hydroxyphenyl)propiony- loxymethyl]cyclohexane, m.p. 115-116°. |
| 10 | N-Octadecyl- thiopropyl/ 0.158 | 0.0079 0.150 | -- | 99-114°/ ATM. 2 hrs. | 120-125°/ 0.1-0.5mm/ 1.25 hrs. | -- | N-octadecylthiopropyl 3-(3, 5-di-t-butyl-4-hydroxy- phenyl)propionate, b.p. 6, 73.78; H, 10.83; Found: 6, 6.15; 8, 73.63; H, 10.65; 9, 6.14. |
| 15 | 1,1,1-tri- methylol- propane/ 0.10 | 0.005 0.33 | DMSO | 77-85°/ 12-14mm/ 5.25 hrs. | 60-80°/ 0.5-1mm/ 2 hrs. | 88-92°/ 0.5mm/ 3 hrs. | 1,1,1-tris-[3-(3,5-di-t- butyl-4-hydroxyphenyl)pro- pionyloxymethyl]-propane, m.p. 65-67°. |

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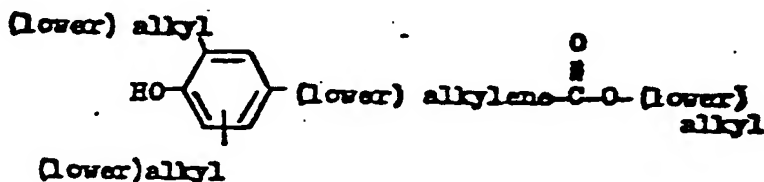
The claims defining the invention are as follows:

1. In the process for the preparation of compounds of the formula:



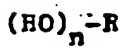
in which R is a non-hydroxylated saturated residual radical of an organic compound having n hydroxy groups, whereby each valence of the radical is on a separate carbon atom selected from the group consisting of straight and branch chain aliphatic hydrocarbons containing from one to thirty carbon atoms whereby n is one to six, cycloaliphatic hydrocarbons containing from five to seven carbon atoms, whereby n is five to seven and straight and branch chain aliphatic mercapto-hydrocarbons containing from four to forty carbon atoms and from one to three non-terminal sulfide links, whereby n is four to six

the steps which comprise treating at least n molar equivalents of an ester of the formula:



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with an alcohol of the formula:



in the presence of from $0.05n$ to $0.15n$ molar equivalents of a hydride of a metal selected from the group consisting of alkali metals and alkaline earth metals at a temperature of from 70°C to 150°C and at a pressure at least as low as the vapor pressure at the reaction temperature of the (lower)alkanol formed.

(27th October, 1965)

2. The process according to claim 1 wherein the reaction is executed in the presence of an alkali-inert non-aqueous organic solvent.

(27th October 1965)

3. The process according to claim 2 wherein the solvent is dimethylsulfoxide, tetrahydrofuran, dioxan, pyridine, dimethylformamide, dimethylacetamide, nitrobenzene or o-nitroanisole.

(27th October 1965)

4. The process according to claim 1 wherein the metal hydride is lithium hydride.

(27th October 1965)

5. The process according to claim 1 wherein the alcohol is ethylene glycol, neopentyl glycol, pentaerythritol or 1,1,1-trimethylolpropane.

(27th October 1965)

6. Manufacture of organic esters substantially as described with reference to any of the foregoing examples 1 to 10.

(27th October 1965)

7. Organic esters of formula 1 whenever prepared or produced by the process of manufacture hereinbefore particularly described in examples 1 to 10.

(27th October, 1965)

DATED this TWENTYFIFTH day of OCTOBER, 1965

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Patent Attorneys for the Applicant
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